

Use of Test Particle Calculations for the Derivation of van der Waals Parameters Used in Force Fields

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ABSTRACT

Test particle calculations are employed to derive van der Waals parameters for methane. It is shown that it is possible to derive these parameters completely based on *ab initio* calculations. The newly derived parameters are tested in molecular dynamics calculations of liquid methane and the results are compared with the results of existing force fields. It is shown that the newly derived parameters perform better in the prediction of the density, the heat of vaporization, and the self-diffusion coefficient of methane. Scaling of the parameters to account for systematic errors in the employed *ab initio* method does not generally improve the parameters with respect to the properties calculated. © 1997 by John Wiley & Sons, Inc.

Introduction

Force fields used in molecular mechanics and dynamics studies of large systems contain terms for nonbond interactions. These terms normally include an expression for the electrostatic energy and either a Lennard–Jones or a Buckingham type expression for repulsive and dispersive energies (van der Waals energy). While there has been a great effort in the past to derive the param-

eters for all other terms in a force field from *ab initio* calculations,^{1–5} nonbond parameters are still largely fitted to experimental data, which may lead to large differences between different force fields as Figure 1 shows. The fit becomes increasingly difficult if force fields are to be derived for systems where experimental data are sparse or where the available data are obtained at room temperature. In the latter case, only molecular dynamics simulations can be used to “derive” the nonbond parameters, because a simple fit will necessarily include temperature effects in the parameters, so that molecular dynamics calculations using these parameters may not give correct results. The use of molecular dynamics simulations to obtain nonbond parameters is a very time-consuming trial-and-error process. It is therefore desirable to

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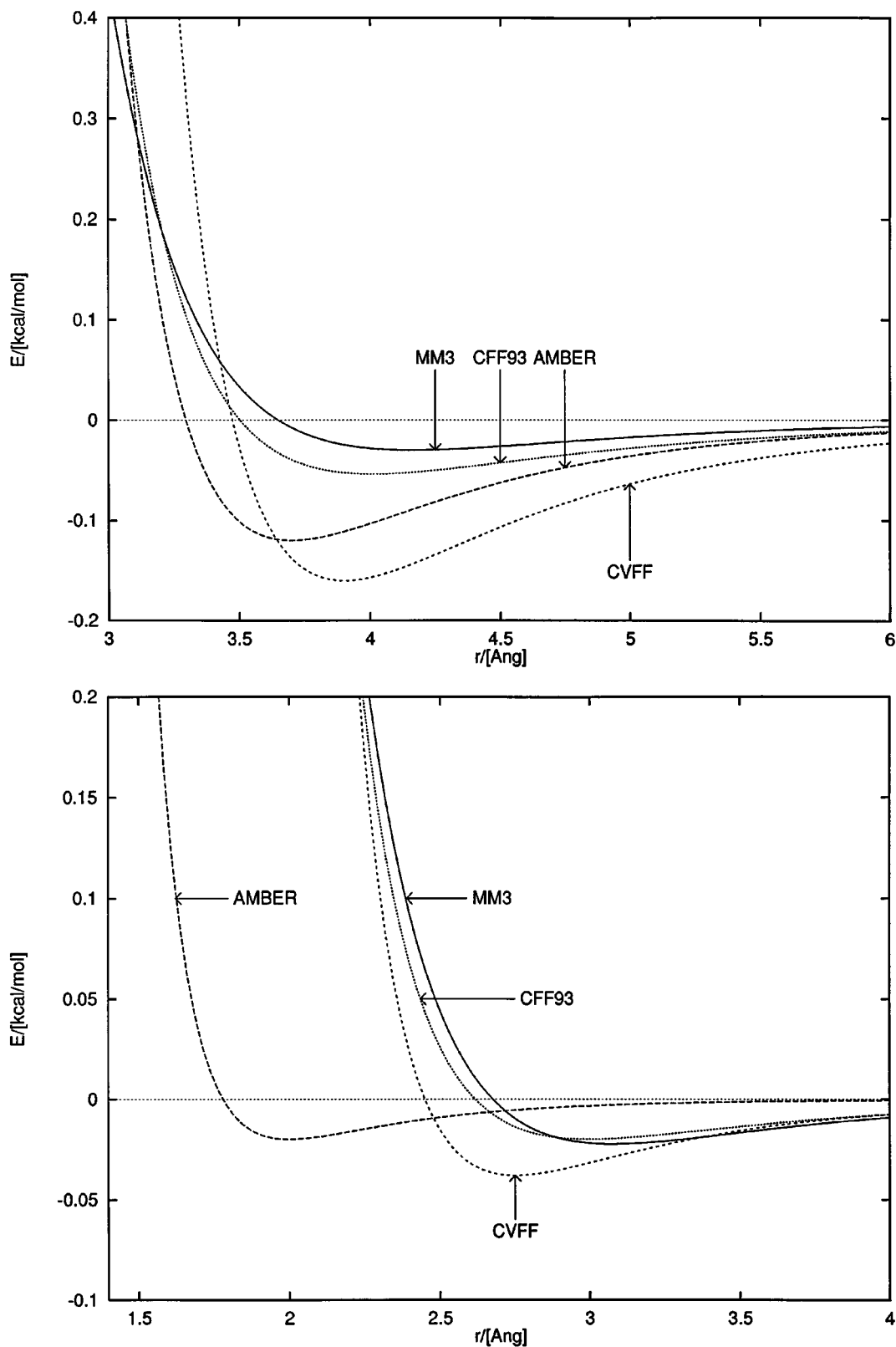


FIGURE 1. The van der Waals energy as function of the distance for CC (top) and HH (bottom) interactions in MM3, AMBER, CVFF, and CFF93 force fields.

have a faster and, hopefully, straightforward approach to the derivation of these parameters.

There have been attempts to derive nonbond parameters by *ab initio* calculations. These attempts focused mainly on the repulsive parameters^{6–8} because these are the more important parameters and it is possible to derive them from SCF calculations. The derivation of dispersive parameters requires more sophisticated methods which include electron correlation and very large basis sets.^{9,10}

Methodology

The total interaction energy between two molecules can be written as¹¹:

$$E = E_{SCF}^{(1)} + E^{(r)} \quad (1)$$

$E_{SCF}^{(1)}$ is known as the first order SCF energy. It can be decomposed into the exchange repulsion and the Coulomb-type interaction. The latter may further be divided into the long-range term and the penetration term. $E_{SCF}^{(1)}$ plays a dominant role in the determination of structural properties of condensed phases and molecular complexes. $E^{(r)}$ contains the remaining higher order terms where polarization and dispersion are the most important contributions.

There has been considerable effort to develop methods to calculate the first order SCF energy and derive parameters for atom–atom repulsion from this energy in the past. The simplest method is to use an uncharged spherical test system to probe the repulsion of an atom in a molecule. The interaction energy obtained by this probing is fitted to a pair potential and atom-based parameters are derived from the pair potential by means of combination rules.^{7,8,12–17} A more sophisticated method which also has been used consists of calculating the interaction energy of two identical molecules in different orientations to each other and fitting the repulsive parameters directly.¹⁸ This approach avoids combination rules in the derivation of the parameters, but is computationally much more demanding since it requires sampling of a six-dimensional space (the relative position in space and orientation of the two molecules). The test particle approach requires only sampling of a three-dimensional space (only the relative position in space) and the test particle can be as simple as an atom.

The derivation of potential parameters for $E^{(r)}$ generally has seen much less work.¹⁹ The dispersion parameters were either fitted to experimental data or experimental data have been used in some empirical rules (e.g., the Slater–Kirkwood formula).^{8,15,20}

In the present study, we will extend the use of a probe to the derivation of dispersion parameters. For this purpose, we will sample the total interaction energy in eq. (1) as a function of the distance and orientation between a test particle and a molecule of interest in a supermolecule approach. Since $E^{(r)}$ contains dispersion which can only be accounted for by methods that include electron correlation we will calculate the interaction energy using Møller–Plesset perturbation theory. The supermolecule approach introduces an additional problem—the basis set superposition error (BSSE), which has not been accounted for in previous work.¹⁹ The BSSE can be corrected by the standard counterpoise correction scheme of Boys and Bernardi.²¹ The theoretical determination of dispersive interaction energies is a very demanding task and it has been shown that large basis sets are necessary to obtain convergence.^{9,10} A careful selection of the basis set is therefore required.

The BSSE corrected interaction energy can be fitted to a Lennard–Jones type potential as it is used in the CFF93 force field^{4,5,22}

$$E = \frac{A_{ij}}{r_{ij}^9} - \frac{B_{ij}}{r_{ij}^6} \quad (2)$$

which can be written, equivalently, as:

$$E = \epsilon_{ij} \left[2 \left(\frac{r_{ij}^*}{r_{ij}} \right)^9 - 3 \left(\frac{r_{ij}^*}{r_{ij}} \right)^6 \right] \quad (3)$$

The ϵ_{ij} and r_{ij}^* in eq. (3) can be calculated from A_{ij} and B_{ij} in eq. (2) by:

$$\begin{aligned} \epsilon_{ij} &= \frac{4B_{ij}^3}{27A_{ij}^2} \\ r_{ij}^* &= \left(\frac{3A_{ij}}{2B_{ij}} \right)^{1/3} \end{aligned} \quad (4)$$

We will use the total interaction energy to determine the parameters for a single atom pair (probed atom/test particle) only, assuming that the total interaction is dominated by the contribution from this pair.

Because the A_{ij} and B_{ij} in eq. (2) are independent from each other, it is easier to use this equation for the actual fit. After fitting the parameters have been converted to the (r^*, ϵ) -representation following eqs. (4). Finally, the combination rules suggested by Waldman and Hagler²³ are used to derive the homonuclear parameters, r_{ii}^* and ϵ_{ii} , from the heteronuclear parameters, r_{ij}^* and ϵ_{ij} , and the test particle parameters, r_{jj}^* and ϵ_{jj} :

$$r_{ii}^* = (2r_{ij}^{*6} - r_{jj}^{*6})^{1/6} \quad (5)$$

$$\epsilon_{ii} = \frac{\epsilon_{ij}^2 (r_{ii}^{*6} + r_{jj}^{*6})^2}{\epsilon_{jj} 4r_{ii}^{*6} r_{jj}^{*6}}$$

Calculations

To derive van der Waals parameters for alkanes we have used methane as the simplest possible molecule. The selection of a test particle, however, is not as straightforward. The results (especially the repulsive parameters) should be largely affected by the size of the test particle. A larger test particle "sees" a different molecular surface than a smaller one. A well-established test particle with the right size for first row elements is a nitrogen atom in its valence state.⁷ Calculations with this test particle are, however, open-shell calculations which would make things more complicated as necessary. We therefore looked at a neon and an argon atom as two closed-shell atoms that may be suitable and checked their performance in comparison with a nitrogen atom in its valence state with respect to repulsive parameters.

Two different sampling techniques were used. First, we chose a certain orientation for the test particle and molecule to be probed and approached the test particle by systematically varying the distance between 10 and 4 atomic units (cf. Fig. 2). Due to the preselected orientation we were able to study the anisotropy of the van der Waals interaction, and will subsequently call this method "anisotropic sampling." Second, we positioned the test particle at a random point in space relative to the molecule probed making sure only that it would be between 10 and 4 atomic units apart from the atom we were sampling and not closer to any other atom in the molecule. With this sampling technique the difference in the interaction caused by anisotropy will be averaged, and we will subsequently call this method "isotropic sampling."

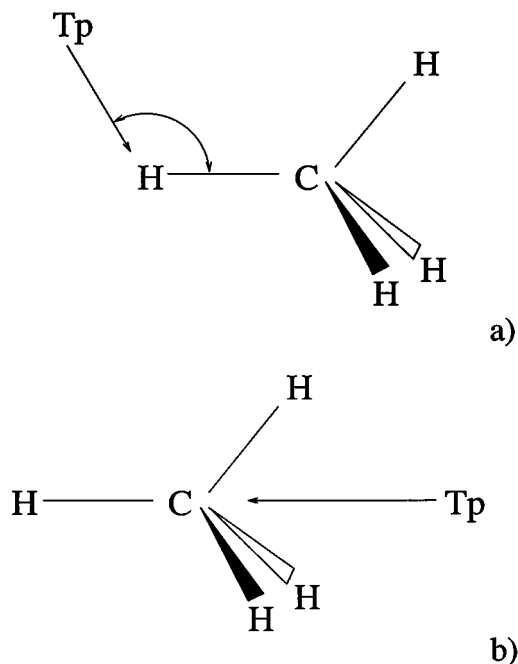


FIGURE 2. Test particle (Tp) probing a hydrogen atom (a) and a carbon atom (b) in methane.

Table I lists the results obtained using anisotropic sampling for two different orientations with the three test particles mentioned above. These results were obtained using first order SCF calculations⁷ with the 6-31G* basis set. While the nitrogen and the neon atom give similar results, the use of the bigger argon atom results in repulsive parameters that are obviously too small. In addition, these results indicate that the repulsive interaction is highly anisotropic, which has also been found by others.²⁴ Since the neon atom is the best choice, according to electronic state *and* size, all of the following results were obtained by using it as the test particle.

The next step was to choose a basis set which would give reasonable results. We calculated the total BSSE corrected interaction energy between two neon atoms[†] and fitted the data. The resulting r^* and ϵ were compared with experimental results and with benchmark calculations. It is well known that polarization and diffuse functions are required to get close to the experimental values.^{9,10} We tried a number of different basis sets of increasing size (cf. Table II) starting from standard basis sets (TZP, TZ2P) and adding polarization and diffuse functions. While the correlation consistent

[†] Available as Supplementary Material.

TABLE I.
Repulsive Parameters for Hydrogen in Methane, A_{HH}
Obtained from First Order SCF Calculations (6-31G*
Basis Set) with a Nitrogen Atom in Its Valence State,
a Neon Atom, and an Argon Atom as Test Particle
(Tp) Dependent upon CHTp Angle and HCHTp
Torsion Angle (kcal · Å⁹ / mol).

$\angle(\text{CHTp})$	$\tau(\text{HCHTp})$	Test particle (Tp)		
		N	Ne	Ar
180	—	295.17	247.82	149.82
90	180	3163.96	2888.41	1537.95

basis sets²⁵ have been used in the past for this kind of study⁹ the aug-cc-pVTZ is still too small. Due to technical limitations in the employed *ab initio* programs, however, we could not go beyond aug-cc-pVTZ. Therefore, we tried to add more polarization and diffuse functions to the standard TZP basis set, resulting in the basis sets labeled as TZ2df + diffuse and TZ3d2f + diffuse. To study the effect of truncating the perturbation expansion after MP2, we repeated aforementioned calculations using MP3 and MP4 with two of the basis sets.

We also tried to use density functional methods which would require much less computer power than Møller–Plesset perturbation theory. Both the B-LYP^{26,27} and the ACM²⁸ methods fail, however,

TABLE II.
Van der Waals Parameters for Neon–Neon Interaction
Determined with Different Basis Sets and Different
Methods of Accounting for Electron Correlation.

Basis set	r_{NeNe}^* / [Å]	ϵ_{NeNe} / [kcal / mol]
MP2		
TZP	3.7798	0.0210
TZ2P	3.6210	0.0308
cc-pVTZ	3.6137	0.0304
aug-cc-pVTZ	3.3782	0.0583
TZ2df + diffuse	3.3859	0.0572
TZ3d2f + diffuse	3.3515	0.0625
MP3		
TZP	3.7225	0.0237
TZ3d2f + diffuse	3.2927	0.0723
MP4		
TZP	3.7851	0.0207
TZ3d2f + diffuse	3.2701	0.0789
Exp. of ref. 41	3.0904	0.0840

to predict a minimum in the interaction energy between two neon atoms. The interaction is entirely repulsive.

We then performed calculations of the total interaction energy of a neon atom and methane with the neon atom at different positions relative to methane using the aug-cc-pVTZ basis set and MP2 as a compromise between accuracy and computational effort. The methane molecule had been geometry optimized before using the same computational methodology. The interaction energies calculated with both sampling methods were BSSE corrected and were fitted to a Lennard–Jones potential [eq. (2)] for the pair test particle/probed atom only. Initial attempts to fit the carbon and hydrogen parameters at the same time (the total interaction energy) yielded parameters that were not physically reasonable. The different parameters obtained using anisotropic sampling were averaged, whereas for isotropic sampling only one set of parameters was fitted.

Finally, the newly derived van der Waals parameters were used in molecular dynamics simulations of liquid methane. These calculations started with a periodic box of the observed density containing 150 methane molecules and used the constant pressure–constant temperature (NPT) ensemble employing Andersen’s algorithm for temperature control²⁹ and Parinello and Rahman’s method for pressure control.³⁰ All internal coordinates of the methane molecules were allowed to change. The simulations used a 8.5 Å cutoff for van der Waals interactions and the Ewald summation for Coulomb interactions. A 1 fs time step was used and the system was equilibrated for 10 ps. Data were then collected for either 200 or 100 ps every 0.1 ps (100 ps were sufficient to get the properties we were interested in converged). From the collected data, the density, the heat of vaporization, and the self-diffusion coefficient were calculated. The self-diffusion coefficient was obtained by using the Einstein equation.³¹ For this purpose, the mean-square-displacement (MSD) was calculated and the function:

$$\frac{\text{MSD}}{6t} = f(1/t) \quad (6)$$

was extrapolated to zero.³² It took approximately 1 ps in all cases to see a random movement starting. In the case of the CVFF force field^{33,34} used for comparison the MSD started to deviate significantly from linearity after it had reached the size of the simulation box. Therefore, only the part of

the MSD between 1 ps and the time it reached the size of the simulation box was taken into account for the determination of the self-diffusion coefficient.

All *ab initio* calculations up to MP2 were carried out using TURBOMOLE.³⁵ The MP3 and MP4 calculations employed the GAUSSIAN 90 program.³⁶ The molecular dynamics simulations were done using DISCOVER³⁷ and the intramolecular parameters as well as charges from the CFF93 force field.^{4,5,22}

Results

Table II contains the van der Waals parameters derived for the neon–neon interaction with different basis sets and different methods of electron correlation. It is clear that even the largest basis set used is still too small to reach convergence. Basis functions of higher angular momentum than f are required as pointed out in ref. 10, but could not be used due to technical limitations in the programs employed. Improvement of the correlation treatment by going from MP2 to MP4 also improves the results significantly. However, the costs of doing MP4 with the largest basis set tested prevented us from using this method in the derivation of van der Waals parameters (a single point BSSE corrected energy for the neon dimer took 4.5 hours on an IBM RS6000/550). As a compromise we used MP2/aug-cc-pVTZ for the test particle calculations on methane.

The orientation of test particle and methane molecule used during anisotropic sampling are best described by the angle C—H—test particle and the torsion angle H—C—H—test particle if the parameters for hydrogen are to be determined (cf. Fig. 2a). We have chosen to use 180°, 135°, and 90° for the angle, whereas the torsion angle in the second case was either 180° or 0°, and in the third case 180° only. The use of a 0° torsion angle in the third case would result in a position of the neon atom where it would be closer to another hydrogen atom than to the probed one. Table III shows the interaction energies obtained (before and after BSSE correction) for each data point and demonstrates the importance of the BSSE correction. Table IV shows the repulsive and dispersive parameters obtained for the neon–hydrogen interaction. It is quite clear from Table IV that both types of interactions are highly anisotropic and that it is necessary to average over these different orientations if

anisotropic effects are not accounted for in the force field and isotropic parameters are the objective. Both arithmetic and geometric averages give very similar results. In contrast, isotropic sampling provides parameters where the r^* is significantly larger and ϵ much smaller, thus resulting in a more repulsive potential. This is caused by the fact that isotropic sampling has more sampling points in the more repulsive region (CHTp angles between 90° and 135°).

By employing the sixth-power combination rule [eq. (5)] on the geometric average for anisotropic sampling, and on the data for isotropic sampling, we obtained the parameters listed in Table V. While the parameters obtained using anisotropic sampling are in good agreement with other force fields (cf. Table V), isotropic sampling gave parameters which are clearly too repulsive and will therefore not be considered any further.

Test particle calculations for the derivation of the van der Waals parameters for the carbon atom are more difficult. Because the carbon atom is surrounded by the four hydrogen atoms its non-bond interactions will always be influenced by electron density from the hydrogen atoms and isotropic sampling is therefore not feasible. The only possible direction under which a test particle can approach the carbon atom is along a CH bond from the opposite side of the hydrogen atom (cf. Fig. 2b). A test particle calculation along this direction gives the van der Waals parameters for carbon listed in Table V. The shielding of the carbon atom by the hydrogen atoms makes the van der Waals parameters for carbon less important.

Table III also contains the interaction energies obtained using the newly derived parameters. These data show that it can be justified to fit the MP2 interaction energy to a single atom pair only. The interaction energy is clearly dominated by the contribution from the probed atom (e.g., from 99% for the smallest distance to 38% for the largest one for 180° for the CHNe angle). It is also interesting to note that, for the case in which the test particle approaches the methane molecule under a CHNe angle of 90°, the total interaction energy calculated from the parameters is close to the MP2 energy, despite the different fitting procedure.

The results obtained using the newly derived van der Waals parameters in molecular dynamics simulations of liquid methane are summarized in Table VI. Employing the same molecular dynamics strategy in a simulation of neon using the experimental van der Waals parameters (cf. Table II) resulted in excellent agreement of the observed

TABLE III.
Interaction Energies Between Methane and a Neon Atom Obtained Using MP2 / aug-cc-pVTZ and Anisotropic Sampling Compared to Results Obtained Using the Unscaled Parameters Derived in This Article.^a

$\angle(\text{CHNe})$	$\tau(\text{HCHNe})$	$r(\text{HNe})$ [au]	E_{MP2} (uncorr.)	E_{MP2} (corr.)	E_{par} (total)	E_{par} (HNe)
180°		4	0.426174	1.206463	2.181824	2.158014
		5	-0.331015	0.008043	-0.015337	0.071776
		6	-0.241421	-0.063967	-0.114858	-0.049079
		7	-0.169788	-0.038270	-0.075366	-0.034211
		8	-0.104002	-0.019510	-0.044176	-0.019069
		9	-0.057280	-0.007752	-0.026018	-0.010514
135°	180°	10	-0.032585	-0.004255	-0.015760	-0.005964
		4	0.939942	1.557629	2.417386	2.158014
		5	-0.271200	0.021686	-0.013060	0.071776
		6	-0.237617	-0.075863	-0.134583	-0.049079
		7	-0.149062	-0.045434	-0.090295	-0.034211
		8	-0.083822	-0.023626	-0.053460	-0.019069
135°	0°	9	-0.045794	-0.012683	-0.031587	-0.010514
		10	-0.025972	-0.007161	-0.019116	-0.005964
		4	0.996642	1.604981	2.431825	2.158014
		5	-0.243287	0.028234	-0.012799	0.071776
		6	-0.221003	-0.075312	-0.135852	-0.049079
		7	-0.139970	-0.046300	-0.091219	-0.034211
90°	180°	8	-0.080049	-0.024483	-0.053994	-0.019069
		9	-0.043798	-0.013002	-0.031880	-0.010514
		10	-0.024906	-0.007256	-0.019276	-0.005964
		4	5.350972	6.318917	8.778779	2.158014
		5	0.065939	0.571127	0.766984	0.071776
		6	-0.380758	-0.096375	-0.120496	-0.049079
		7	-0.285595	-0.094059	-0.151920	-0.034211
		8	-0.179011	-0.051600	-0.100056	-0.019069
		9	-0.102714	-0.026372	-0.060115	-0.010514
		10	-0.056295	-0.014381	-0.035919	-0.005964
		$r(\text{CNe})$ [au]				E_{par} (CNe)
		4	15.965475	17.345958	27.549898	17.356261
		5	1.118590	1.796377	2.359318	1.697867
		6	-0.355612	-0.014300	0.001148	0.146434
		7	-0.323696	-0.107346	-0.162383	-0.027080
		8	-0.205688	-0.060837	-0.113525	-0.033607
		9	-0.120428	-0.029766	-0.067811	-0.022971
		10	-0.065593	-0.016200	-0.039919	-0.014380

^a E_{MP2} (uncorr.) is the MP2 energy before BSSE correction, E_{MP2} (corr.) is the BSSE corrected MP2 energy, E_{par} (total) is the total energy obtained with the derived parameters, and E_{par} (HNe) [(CNe)] is the interaction energy between the probed hydrogen [carbon] atom and the neon atom obtained with the derived parameters. All energies are in kilocalories per mole.

and calculated density. To compare the performance of the new approach with existing force fields the same molecular dynamics simulations were performed with the CVFF,^{33,34} AMBER,³⁸ and CFF93^{4,5,22} force fields. For the CFF93 force field, scaled van der Waals parameters were used,³⁹ which improve its predictions for the bulk proper-

ties of liquids. While the AMBER force field was unable to predict the existence of liquid methane (the box “exploded” already during equilibration), the CVFF and CFF93 force fields gave reasonable results. Tsuzuki *et al.* have also calculated the same properties using the MM2 and MM3 force fields as well as one of their own.¹⁸ Their results

TABLE IV.
Van der Waals Parameters for the Neon–Hydrogen
(in Methane) Interaction Obtained Using MP2 /
aug-cc-pVTZ and Anisotropic As Well As Isotropic
Sampling.

Sampling	$\angle(\text{CHNe})$	$\tau(\text{HCHNe})$	r_{HNe}^* ^a	ϵ_{HNe} ^b
Anisotropic	180		3.0220	0.0505
	135	180	3.0506	0.0582
	135	0	3.0649	0.0567
	90	180	3.6334	0.0347
	arithmetic average		3.1927	0.0500
	geometric average		3.1831	0.0490
Isotropic	random	random	3.4776	0.0230

^a Values expressed in angstroms.
^b Values expressed in kilocalories per mole.

are included in Table VI, but it should be noted that these calculations also used a cutoff for the Coulomb interaction, which could lead to some differences. Some of the properties were also evaluated by Nagy *et al.* in their comparison of different force fields.⁴⁰ They used Monte Carlo calculations and their results basically agree with the results of Tsuzuki *et al.* Table VI clearly indicates that the newly derived parameters perform significantly better than the parameters used in all previous force fields. The calculated density is slightly improved with the new parameters. The heat of vaporization shows a much more dramatic improvement. The self-diffusion coefficient, on the other hand, is predicted to be worse than with the CVFF force field, but still much better than with MM2 or MM3.

TABLE VI.
Results of Molecular Dynamics Simulations of Liquid Methane Using van der Waals Parameters Derived in This
Study in Comparison with Literature Results.^a

Parameters	ρ	ΔH_{vap}	D
MM2 (ref. 18)	0.539 (27%)	3.76 (92%)	1.1 (−80%)
MM3 (ref. 18)	0.363 (−14%)	1.52 (−22%)	8.5 (57%)
CVFF	0.362 (−15%)	1.55 (−21%)	5.3 (−2%)
CFF93 (scaled, ref. 39)	0.350 (−17%)	1.39 (−29%)	9.3 (72%)
Ref. 18, model III	0.380 (−10%)	1.68 (−14%)	6.5 (20%)
This work (unscaled)	0.373 (−12%)	2.02 (3%)	4.5 (−17%)
This work (r^* scaled)	0.415 (−2%)	2.05 (5%)	2.8 (−48%)
This work (ϵ scaled)	0.384 (−9%)	2.34 (19%)	2.9 (−46%)
Observed	0.424 ^b	1.96 ^b	5.4 ^c

^a Density = ρ (g/cm³); the heat of vaporization = ΔH_{vap} (kcal/mol); self-diffusion coefficient = D (in 10⁹ m²/s).
^b From ref. 42.
^c From ref. 43.

TABLE V.
van der Waals Parameters Derived in This Study
Compared with Parameters of Other Force Fields.

i	$r_{ii}^*/[\text{\AA}]$	$\epsilon_{ii}/[\text{kcal/mol}]$
This study, anisotropic sampling, unscaled		
C	4.3489	0.0374
H	2.8994	0.0506
r^* scaled		
C	4.1489	0.0374
H	2.7660	0.0506
ϵ scaled		
C	4.3489	0.0394
H	2.8994	0.0534
This study, isotropic sampling		
H	3.5645	0.0093
CVFF ³³		
C	4.3500	0.0390
H	2.7500	0.0380
CFF93, scaled ³⁹		
C	3.8536	0.0617
H	2.8782	0.0228

From the test calculations performed on neon to find a suitable basis set we know that MP2/aug-cc-pVTZ underestimates ϵ and overestimates r^* (cf. Table II). We can therefore try to improve the parameters by scaling. The scaling factors can be derived from a comparison of experimental data and calculations of noble gas dimers. Woon has published a large number of calculations using different correlation-consistent basis sets including the aug-cc-pVTZ basis set used in our study.⁹ Table VII compares Woon’s results with experi-

TABLE VII.
Comparison of van der Waals Parameters Calculated with MP2 / aug-cc-pVTZ and Experimental Data and Scaling Factors Derived from This Comparison.

Dimer	$r^*/[\text{\AA}]$		Scaling factor	$\epsilon/[\text{kcal/mol}]$		Scaling factor
	Calc. ^a	Obs.		Calc. ^a	Obs.	
He ^b	3.1333	2.9687	0.9475	0.0112	0.0217	1.9330
Ne ^c	3.2947	3.0904	0.9380	0.0366 ^e	0.0840	2.2945
Ar ^d	3.8471	3.7572	0.9766	0.2414	0.2847	1.1795
Average			0.9540			1.5176 ^f

^a From ref. 9.

^b Observed results from ref. 44.

^c Observed results from ref. 41.

^d Observed results from ref. 45.

^e The ϵ for Ne from the study by Woon is obviously wrong. Our own calculation using the same basis set results in 0.0583 kcal/mol, which brings the scaling factor with 1.4403 in line with the other results.

^f Average calculated using scaling factor from footnote e for neon.

mental data and lists scaling factors. The scaling factors obtained for ϵ are probably too large if we consider that the unscaled van der Waals parameters already give quite good results in molecular dynamics simulations. They also vary significantly with different noble gases. We therefore used a scaling factor of 1.06 for ϵ . The scaling factors for r^* are much closer to each other. We therefore used the average of the three scaling factors in Table VII to scale our r^* . The results obtained in molecular dynamics simulations of liquid methane using the scaled van der Waals parameters are included in Table VI. Scaling of r^* significantly improves the density, has not much effect on the heat of vaporization, and makes the self-diffusion coefficient worse. Scaling of ϵ slightly improves the density, but makes the heat of vaporization and the self-diffusion coefficient worse. It is clear from this result that using a scale factor for ϵ of the size derived in Table VII would not be suitable. It is somewhat surprising that the scaling does not improve the performance of the parameters. Because the effect on different properties calculated is opposite while scaling (the density improves, the self-diffusion coefficient worsens), it can only be deduced that the functional form used for nonbond interactions is inadequate. We have seen, during the derivation of the parameters, that anisotropic effects play an important role. Therefore, it seems desirable to include these effects into a force field's functional form. It should also be remembered that polarization is an important part of $E^{(r)}$ which has not been accounted for. Other effects, like three-body effects, or charge flux will also have an influence on the results, but are also not included in current force fields.

Conclusions

We have shown that it is possible—with a moderate effort—to derive reliable van der Waals parameters based solely on *ab initio* calculations. Parameters obtained this way outperform parameters fitted to experimental data when it comes to calculating macroscopic properties using molecular dynamics simulations. This is somewhat surprising, because we know that the method used to derive the parameters causes rather large systematic errors. A compensation for these errors by scaling does not necessarily improve the performance of the parameters with respect to all calculated properties. This is obviously related to inadequacies in the functional form used to represent the nonbond interactions (e.g., neglect of anisotropy and polarization).

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References

1. J. R. Maple, U. Dinur, and A. T. Hagler, *Proc. Natl. Acad. Sci. USA*, **85**, 5350 (1988).
2. J. R. Maple, T. S. Thatcher, U. Dinur, and A. T. Hagler, *Chem. Des. Automat. News* **5**, 9, 10 (1990).

3. K. Palmö, L.-O. Pietilä, and S. Krimm, *J. Comput. Chem.*, **12**, 385 (1991).
4. J. R. Maple, M.-J. Hwang, T. P. Stockfisch, U. Dinur, M. Waldman, C. S. Ewig, and A. T. Hagler, *J. Comput. Chem.*, **15**, 162 (1994).
5. A. T. Hagler and C. S. Ewig, *Comp. Phys. Commun.*, **84**, 131 (1994).
6. U. Dinur and A. T. Hagler, *J. Am. Chem. Soc.*, **111**, 5149 (1989).
7. H.-J. Böhm and R. Ahlrichs, *J. Chem. Phys.*, **77**, 2028 (1982).
8. H.-J. Böhm, R. Ahlrichs, P. Scharf, and H. Schiffer, *J. Chem. Phys.*, **81**, 1389 (1984).
9. D. E. Woon, *J. Chem. Phys.*, **100**, 2838 (1994).
10. T. van Mourik and J. H. van Lenthe, *J. Chem. Phys.*, **102**, 7479 (1995).
11. P. Claverie, In *Intermolecular Interactions: From Diatomics to Biopolymers*, B. Pullman, Ed., John Wiley & Sons, New York, 1978.
12. H.-J. Böhm, C. Meissner, and R. Ahlrichs, *Mol. Phys.*, **53**, 651 (1984).
13. K. P. Sagarik, R. Ahlrichs, and S. Brode, *Mol. Phys.*, **57**, 1247 (1986).
14. K. P. Sagarik and R. Ahlrichs, *Chem. Phys. Lett.* **131**, 74 (1986).
15. K. P. Sagarik and R. Ahlrichs, *J. Chem. Phys.*, **86**, 5117 (1987).
16. J.-R. Hill and J. Sauer, *J. Phys. Chem.*, **98**, 1238 (1994).
17. J.-R. Hill and J. Sauer, *J. Phys. Chem.*, **99**, 9536 (1995).
18. S. Tsuzuki, T. Uchimaru, K. Tanabe, and S. Kuwajima, *J. Phys. Chem.*, **98**, 1830 (1994).
19. B. Amaee and W. Byers Brown, *Chem. Phys.*, **174**, 351 (1993).
20. F. A. Momany, L. M. Carruthers, R. F. McGuire, and H. A. Scheraga, *J. Phys. Chem.*, **78**, 1595 (1974).
21. S. F. Boys and F. Bernardi, *Mol. Phys.*, **19**, 553 (1970).
22. M.-J. Hwang, T. P. Stockfisch, and A. T. Hagler, *J. Am. Chem. Soc.*, **116**, 2515 (1994).
23. M. Waldman and A. T. Hagler, *J. Comput. Chem.*, **14**, 1077 (1993).
24. A. J. Stone and C.-S. Tong, *J. Comput. Chem.*, **15**, 1377 (1994).
25. T. H. Dunning, Jr., *J. Chem. Phys.*, **90**, 1007 (1989).
26. A. D. Becke, *Phys. Rev.*, **A38**, 3098 (1988).
27. C. Lee, W. Yang, and R. G. Parr, *Phys. Rev.*, **B37**, 785 (1988).
28. A. D. Becke, *J. Chem. Phys.*, **98**, 5648 (1993).
29. H. C. Andersen, *J. Chem. Phys.*, **72**, 2384 (1980).
30. M. Parinello and A. Rahman, *J. Appl. Phys.*, **52**, 7182 (1981).
31. P. W. Atkins, *Physical Chemistry*, Oxford University Press, Oxford, UK, 1987.
32. P. Demontis, G. B. Suffritti, A. Alberti, S. Quartieri, E. S. Foïs, and A. Gamba, *Gazz. Chim. Ital.*, **116**, 459 (1986).
33. A. T. Hagler, E. Huler, and S. Lifson, *J. Am. Chem. Soc.*, **96**, 5319 (1974).
34. S. Lifson, A. T. Hagler, and P. Dauber, *J. Am. Chem. Soc.*, **101**, 5111 (1979).
35. R. Ahlrichs, M. Bär, S. Brode, M. Ehrig, F. Haase, M. Häser, H. Horn, C. Kölmel, A. Schäfer, H. Schiffer, and P. Weis, Program TURBOMOLE, Universität Karlsruhe (TH), 1992.
36. M. J. Frisch, M. Head-Gordon, G. W. Trucks, J. B. Foresman, H. B. Schlegel, K. Raghavacharia, M. Robb, J. S. Binkley, C. Gonzalez, D. J. Defrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, S. Topiol, and J. A. Pople, GAUSSIAN 90, Revision I, Gaussian, Inc., Pittsburgh, PA, 1990.
37. Biosym/MSI, Program DISCOVER, San Diego, CA, 1995.
38. S. J. Weiner, P. A. Kollman, D. A. Case, U. C. Singh, C. Ghio, G. Alagona, S. Profeta, and P. Weiner, *J. Am. Chem. Soc.*, **106**, 765 (1984).
39. H. Sun, personal communication, 1995.
40. J. Nagy, D. F. Weaver, and V. H. Smith, Jr., *J. Phys. Chem.*, **99**, 8058 (1995).
41. R. A. Aziz and M. J. Slamam, *Chem. Phys.*, **130**, 187 (1989).
42. F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun, and G. C. Pimentel, *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds*, Carnegie Press, Pittsburgh, PA, 1953.
43. K. R. Harris and N. J. Trappeniers, *Physica*, **104A**, 262 (1980).
44. R. A. Aziz and M. J. Slamam, *J. Chem. Phys.*, **94**, 8047 (1991).
45. R. A. Aziz and H. H. Chen, *J. Chem. Phys.*, **67**, 5719 (1977).